

Two isomorphous imidazole (Him) complexes: $[MCl_2(Him)_2(H_2O)_2]$ ($M = Co$ and Ni)

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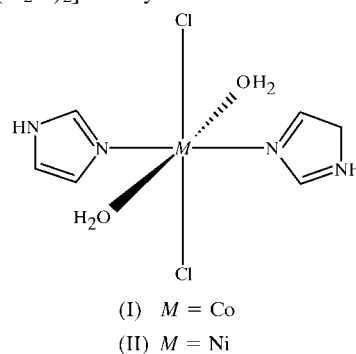
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The structures of aquadichlorobis(1*H*-imidazole)cobalt(II), $[CoCl_2(Him)_2(H_2O)_2]$ (Him is 1*H*-imidazole, $C_3H_4N_2$), (I), and aquadichlorobis(1*H*-imidazole)nickel(II), $[NiCl_2(Him)_2(H_2O)_2]$, (II), are isomorphous and consist of monomers with inversion symmetry. The three monodentate ligands (imidazole, chlorine and aqua), together with their symmetry equivalents, define almost perfect octahedra. Hydrogen-bonding interactions *via* the imidazole and aqua H atoms lead to a three-dimensional network.

Comment

The study of imidazole as a complexing agent has for years been a matter of active interest, mainly because imidazole is involved in important biological processes, but also because it forms a number of inorganic materials with interesting structural and magnetic properties (*e.g.* Atria *et al.*, 1999). While attempting to synthesize new cobalt and nickel systems of high nuclearity, we unwittingly came across two very simple though structurally unreported isomorphous monomers, *viz.* $[MCl_2(Him)_2(H_2O)_2]$ ($M = Co$ and Ni , and Him is 1*H*-imidazole). In spite of its simplicity, the $[MCl_2(Him)_2(H_2O)_2]$ group (M is a transition metal) does not seem to be very common; it has been mentioned in the literature as being detected in solution [*viz.* NMR evidence of the appearance of the Ru homolog as a solvation product of the antitumoral $RuCl_4(Him)_2$; Anderson & Beauchamp, 1995], but no structural report on the neutral molecule was found in a search of the latest release of the Cambridge Structural Database (CSD; Allen, 2002). There are, however, a few appearances of closely related ions with similar ligands in both anionic $\{[RuCl_4(Him)_2]^{2-}\}$; Keppler *et al.*, 1987; Anderson & Beauchamp, 1995; Mestroni *et al.*, 1998; Mura *et al.*, 2001] and cationic $\{[Ni(Him)_2(H_2O)_4]^{2+}\}$; Polyakova *et al.*, 2000] forms. We report here the structures of the

cobalt, (I), and nickel, (II), isologs of the (presumably larger) $[MCl_2(Him)_2(H_2O)_2]$ family.



The structures of (I) and (II) are composed of monomeric units built up around a symmetry center on which the metal atom lies (Fig. 1). The metal atom is surrounded by six monodentate ligands, *viz.* an *N*-coordinated imidazole group, a chloride anion and a water molecule, and their symmetry-related counterparts. The absence of any steric hindrance due to chelation or bridging effects results in an almost perfect octahedral cation environment, with angles differing from an ideal value of 90° by less than 0.6% in (I) and 1.2% in (II), and with 180° angles being imposed by symmetry. Coordination distances are normal and similar to the average calculated for the same monodentate ligands in other hexacoordinated Co and Ni complexes. The bonds involving the N_{Him} and O_{aq} atoms fall within 0.5% of the CSD average, while larger differences were found in the Cl bonding distances [$Co-Cl = 2.5004(4)$ Å in (I) and $Ni-Cl = 2.4665(5)$ Å in (II); CSD averages are 2.37 (11) and 2.42 (8) Å, respectively].

In both (I) and (II), the imidazole groups depart from planarity by less than 0.02 Å; the internal geometries are as expected, with the $N1=C3$ and $C1=C2$ bond lengths corresponding exactly to typical double-bond lengths. The ligands

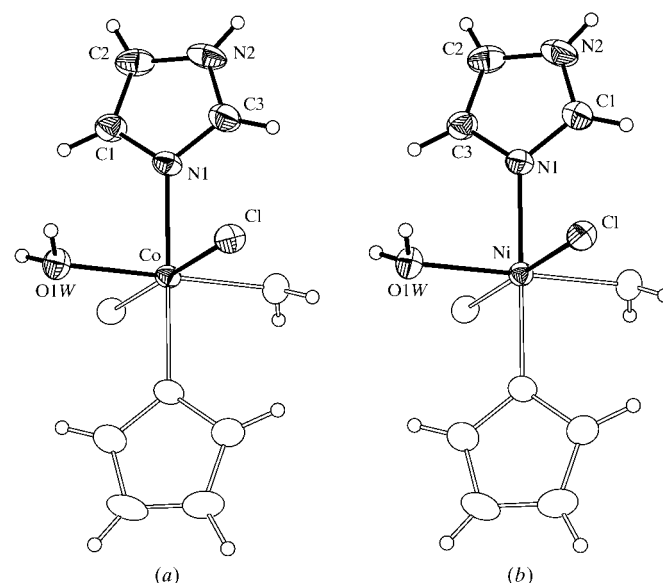


Figure 1
Molecular diagrams for (a) compound (I) and (b) compound (II), showing displacement ellipsoids at the 50% probability level.

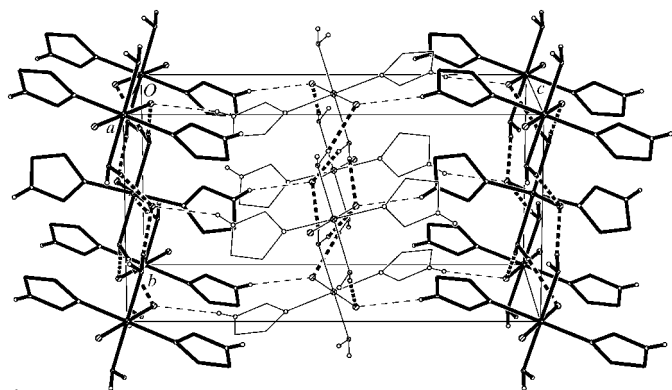


Figure 2

A view of the crystal packing in (I) and (II), showing the two-dimensional structures internally linked by OW–H...Cl hydrogen bonds (heavy broken lines), with N–H...Cl hydrogen bonds joining the planes (light broken lines).

bind to the cations in a slightly angled manner, subtending dihedral angles of 8.3 (1)° (in both structures) to the perfectly planar basal planes and almost bisecting the dihedral angles subtended by the lateral coordination planes [angles with respect to the N1–M–Cl1 and N1–M–O1W planes are, respectively, 49.0 (1) and 41.7 (1)° for (I), and 49.5 (1) and 41.6 (1)° for (II)].

The three potentially active H atoms (H2N, H1WA and H1WB) are engaged in hydrogen bonds with the Cl atom, which acts as the sole acceptor for all three interactions (Tables 1 and 2). The bond involving atom H2N is of medium strength compared with the 19 cases in the CSD for which the H...Cl distance between a coordinated imidazole group and a coordinated chlorine unit is smaller than the sum of their van der Waals radii [2.543 (17) Å in (I), 2.572 (15) Å in (II) and 2.52 (17) Å (mean for 19 cases) in the CSD]. Bonds involving the aqua H atoms seem to be only slightly stronger than average [2.340 (10) and 2.336 (11) Å in (I), 2.387 (11) and 2.358 (11) Å in (II), and 2.42 (18) Å (mean for 350 cases) in the CSD].

These aqua interactions link monomers along [100] and [010], thus defining two-dimensional arrays parallel to (001) [the shortest M...M distances are 6.081 (1) and 6.044 (1) Å in (I) and (II), respectively]. Fig. 2 depicts these arrays in projection (alternately drawn in heavy and light full lines, in order to distinguish between them). The aqua hydrogen bonds (heavy broken lines) are clearly visible. These two-dimensional structures, in turn, are linked *via* the imino hydrogen bonds (light broken lines), thus defining a complex three-dimensional network.

Experimental

Crystals of (I) were obtained from an equimolar solution of CoCl₂·6H₂O (0.01 mmol, 0.2379 g) and imidazole (0.01 mmol, 0.6808 g) in methanol (35 ml). The solution was refluxed for 30 min and, after being left for a few days at room temperature, pink polyhedral crystals appeared. The same procedure, with NiCl₂ (0.01 mmol, 0.1655 g) as a starting material, was used to obtain crystals of (II) in the form of green polyhedra. In both cases, the solvent was oxygenated for 10 min.

Compound (I)

Crystal data

[CoCl₂(C₃H₄N₂)₂(H₂O)₂]
M_r = 302.03
 Orthorhombic, *Pbca*
a = 9.1894 (10) Å
b = 7.9653 (9) Å
c = 15.6683 (17) Å
V = 1146.9 (2) Å³
Z = 4
D_x = 1.749 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 247 reflections
 θ = 3.0–25.1°
 μ = 1.95 mm⁻¹
T = 293 (2) K
 Plate, pink
 0.20 × 0.10 × 0.04 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS in S_AI_NT-NT; Bruker, 2002)
T_{min} = 0.80, *T_{max}* = 0.93
 6204 measured reflections

1304 independent reflections
 963 reflections with *I* > 2σ(*I*)
R_{int} = 0.077
 θ_{\max} = 28.1°
h = -11 → 11
k = -6 → 10
l = -15 → 20

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.025
wR(*F*²) = 0.061
S = 0.94
 1304 reflections
 94 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.023P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.004$
 $\Delta\rho_{\max} = 0.28 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.26 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bonding geometry (Å, °) for (I).

| <i>D</i> –H... <i>A</i> | <i>D</i> –H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> –H... <i>A</i> |
|------------------------------|-------------|---------------|-----------------------|-------------------------|
| N2–H2N...Cl ⁱ | 0.848 (10) | 2.543 (17) | 3.2461 (16) | 141 (2) |
| O1W–H1WA...Cl ⁱⁱ | 0.858 (9) | 2.340 (10) | 3.1923 (14) | 172 (2) |
| O1W–H1WB...Cl ⁱⁱⁱ | 0.841 (9) | 2.336 (11) | 3.1678 (14) | 170 (2) |

Symmetry codes: (i) $\frac{3}{2} - x, -y, z - \frac{1}{2}$; (ii) $\frac{3}{2} - x, \frac{1}{2} + y, z$; (iii) $x - \frac{1}{2}, \frac{1}{2} - y, 1 - z$.

Compound (II)

Crystal data

[NiCl₂(C₃H₄N₂)₂(H₂O)₂]
M_r = 301.80
 Orthorhombic, *Pbca*
a = 9.1185 (7) Å
b = 7.9344 (6) Å
c = 15.5636 (12) Å
V = 1126.02 (15) Å³
Z = 4
D_x = 1.780 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 123 reflections
 θ = 3.0–24.7°
 μ = 2.18 mm⁻¹
T = 293 (2) K
 Plate, green
 0.20 × 0.20 × 0.02 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS in S_AI_NT-NT; Bruker, 2002)
T_{min} = 0.82, *T_{max}* = 0.96
 6136 measured reflections

1301 independent reflections
 1018 reflections with *I* > 2σ(*I*)
R_{int} = 0.043
 θ_{\max} = 28.0°
h = -11 → 8
k = -10 → 10
l = -19 → 18

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.028$

$wR(F^2) = 0.062$

$S = 1.27$

1301 reflections

94 parameters

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0210P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.005$$

$$\Delta\rho_{\max} = 0.50 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.36 \text{ e } \text{\AA}^{-3}$$

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$) for (II).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---------------------------|------------|-------------|-------------|---------------|
| $N2-H2N\cdots Cl^i$ | 0.847 (9) | 2.553 (15) | 3.2591 (17) | 141.6 (18) |
| $O1W-H1WA\cdots Cl^{ii}$ | 0.850 (9) | 2.368 (11) | 3.2077 (14) | 170 (2) |
| $O1W-H1WB\cdots Cl^{iii}$ | 0.847 (15) | 2.340 (11) | 3.1744 (15) | 168 (2) |

Symmetry codes: (i) $\frac{3}{2} - x, -y, z - \frac{1}{2}$; (ii) $\frac{3}{2} - x, \frac{1}{2} + y, z$; (iii) $x - \frac{1}{2}, \frac{1}{2} - y, 1 - z$.

H atoms attached to C atoms were added at calculated positions and allowed to ride on their parent atoms; H atoms involved in hydrogen bonding (those attached to atoms N2 and O1W) were found in a difference Fourier synthesis and refined with restrained distances [$0.85(1) \text{\AA}$] to the host atoms. The CCDC package (Version 5.24 of November 2002 and updates; Allen, 2002) was used for searches.

For both compounds, data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SMART-NT*; data reduction: *SAIN-NT* (Bruker, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick,

1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1994); software used to prepare material for publication: *SHELXTL/PC*.

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